(12) UK Patent Application (19) GB (11) 2 221 916 (13) A

(43) Date of A publication 21.02.1990

(21) Application No 8825093.1

(22) Date of filing 26.10.1988

(30) Priority data
(31) 233788 (32) 19.08.1988 (33) US

(71) Applicant
Petrolite Corporation

(Incorporated in the USA - Delaware)

369 Marshall Avenue, Saint Louis, Missouri 63119, United States of America

(72) Inventors
Timothy J Baker
William P Cottom
Jeffrey R Zerr

(74) Agent and/or Address for Service
Edward Evans & Co
Chancery House, 53-64 Chancery Lane, London, WC2A 1SD, United Kingdom

(51) INT CL⁴
C08J 3/06, C08L 71/00, C09D 11/02

(52) UK CL (Edition J)
C3R RSX R27K8F
C3L LDK
C3V VAD
C3W W100 W324
U1S S1390 S2241

(56) Documents cited
GB 2185746 A GB 1438012 A GB 1438011 A
GB 1270987 A GB 0950844 A GB 0857434 A
GB 0380431 A US 3563910 A

(58) Field of search
UK CL (Edition J) C3K KJA, C3L LDK, C3R RSX, C3V VAD
INT CL⁴ C08L, C09D

(54) Aqueous dispersions of alkoxylated alcohols and printing inks containing the dispersions

(57) Water-based dispersions usable as printing ink additives are prepared using high molecular weight, linear, alkoxylated, primary alcohols having an average chain length in the hydrocarbon portion of the alcohol of from about 22 to about 150 carbon atoms.

The preparation comprises slowly adding the alkoxylated alcohol, which has been heated to a temperature above its melting point, to water which has also been heated, and thereafter cooling the dispersion while stirring.

GB 2 221 916 A

DISPERSIONS OF SOLIDS IN AQUEOUS SYSTEMS

Field of the Invention

1. Background of the Invention

This invention relates to dispersions of solids in aqueous systems. More particularly, this invention relates to water-based printing ink additive dispersions which may be waxes and/or polymers.

There are four (4) general classes of printing inks. There are letter press and lithographic inks, also known as oil inks or paste inks, and there are flexographic and rotogravure inks, also known as solvent or liquid inks. This invention is concerned with a particular class of flexographic and rotogravure inks which are water-based. Although these inks have certain characteristics in common with inks used in other printing processes, they form a distinct class because of the character of their printing processes, their applications and formulations. The main distinction of flexographic and rotogravure inks is that they are of low viscosity compared to other classes of printing inks.

Flexographic and rotogravure inks have, in the past, been prepared by dissolving or dispersing pigments or other colorants in volatile solvents such as alcohols, ketones and hydrocarbons. Due to environmental problems associated with the manufacture of inks formulated with volatile solvents, water-based flexographic and rotogravure inks are becoming more important.

In flexographic printing, a form of rotary letter press uses a flexible plate, such as rubber, and fluid inks. Originally, flexographic printing was used for paper bag printing but subsequently proved suitable for printing almost any kind of flexible packaging material. Flexographic inks generally consist of pigment dispersed in a vehicle made by dissolving one or more resins in a solvent such as a volatile solvent, or water. The water-based flexographic inks are widely used on

paper and paper board. The vehicles for water-based inks are usually made from acrylic copolymers, acidic rosin esters, shellac, acidic styrene copolymers and additives such as waxes. The advantages of water based inks include good press stability and printability, absence of fire hazard and volatile solvent emissions, convenience and the economy of water as a diluent and for wash-up. Since the water based inks do not use volatile solvents, their use is gaining favor over the use of solvent-based inks.

Rotogravure inks have three essential ingredients: a pigment, a resin, a polymer or wax additive and a solvent. As in flexographic inks, water-based rotogravure inks are gaining favor over solvent-based inks because of environmental and worker hazard considerations.

In general, water-based inks are a mixture of water, resin, emulsifier or dispersing agent, a pigment and a polymer or wax additive. One of the problems associated with water-based inks, is that the water-based additive systems, containing polymers, waxes and other ingredients to enhance various characteristics of the ink, have not been made which contained above about 30% solids using as much as 25% dispersant based on the total additive volume.

2. Prior Art

U.S. Patent No. 2,925,349 discloses a polish which utilizes alcohols having up to 20 carbon atoms as dispersants. Such alcohols may be oxyethylated.

U.S. Patent No. 3,533,811 discloses a water-based printing ink comprising a water-missable organic solvent, film forming resins which are soluble in the water-missable solvent, pigment, soluble protein, a polymer latex and a volatile base. The water-missable organic solvents which are used are lower aliphatic alcohols and the lower alkylene glycols and their esters and ethers.

U.S. Patent No. 3,563,910 discloses alkoxylated alcohols having up to 38 carbon atoms as emulsifiers for water/hydrocarbon mixtures.

U.S. Patent No. 3,884,707 discloses a water-based ink comprising a basic dye, water, an organic solvent and a resin. The organic solvents employed are, for example, ethylene glycol and its ethers.

U.S. Patent No. 4,686,260 discloses a process for preparing a polymer emulsion for a water-based ink which contains colloidally suspended polymer. The emulsifiers used are anionic, cationic or nonionic emulsifiers or mixtures thereof such as a variety of alcohols and ethylene oxide derivatives of long-chained carboxylic acids such as lauric, myristic, palmitic, oleic and stearic acids. Also, analogous ethylene oxide condensates of long-chained alcohols, such as octyl, decyl, stearyl and cetyl alcohols are used.

Summary of the Invention

In accordance with the present invention, it has been found that certain high molecular weight, linear, alkoxylated primary alcohols provide superior dispersant characteristics to water-based ink additives systems containing waxes and polymers, particularly for use in water-based flexographic and rotogravure inks. The inks to which the water-based additive systems of the present invention are added have improved adhesion, gloss and slip properties.

Accordingly, an object this invention is to prepare high solids content water-based ink additive dispersions containing only water and the alkoxylated alcohol. Such dispersions are suitable as ink additive systems and can be used to replace present water-based additive systems containing conventional polymers and waxes.

Another object of the invention is to provide a process for preparing high solids content ink additive systems containing water and high molecular weight, linear, alkoxylated primary alcohols.

A further object of the invention is to prepare a water-based ink, containing an ink additive system which contains a high molecular weight, linear, alkoxylated primary alcohol.

Specific Embodiments of the Invention

It has been found that high molecular weight, linear, alkoxylated alcohols having an average chain length in the hydrocarbon portion of the alcohol of from about 24 to about 150 carbon atoms, preferably from about 40 to about 90 carbon atoms, especially about 50 carbon atoms, are superior dispersants for forming high solids level additive dispersions which are useful in water-based systems, particularly in water-based ink additive systems.

The dispersants used in formulating the water-based ink additive systems of the invention are represented by the formula:

$$CH_3(CHCH)_x\,CH_2O(CH_2CHO)_n\,H$$

(with R and R_1 on the CHCH groups and R_2 on the CH_2CHO groups)

wherein R and R_1 individually represent hydrogen or the same or different lower alkyl groups of from about 3 to about 7 carbon atoms; R_2 represents hydrogen or a methyl group; x represents a number of from about 10 to about 75, preferably from about 20 to about 50, and represents the average number of carbon atoms in the hydrocarbon portion of the chain; and n represents the number of oxyalkylene groups present in the molecule.

The dispersants are prepared by alkoxylation of alcohols represented by the formula:

$$CH_3(CHCH)_xCH_2OH$$

(with R and R_1 on the CHCH groups)

wherein R, R_1 and x are defined above. Alkoxylating agents include ethylene oxide, propylene oxide and mixtures thereof. The starting materials can be readily

alkoxylated with the described alkylene oxides using typical base catalysts such potassium hydroxide, sodium hydroxide, sodium ethoxide, potassium t-butoxide, sodium hydride or sodium or potassium metals. The reaction is normally conducted under pressures of 0 to 60 psig and at temperatures of 100° to 180°C. Higher temperatures are normally avoided to prevent side reactions, i.e., rearrangement of the epoxide to form unsaturated alcohols.

By varying the molecular weight of the starting alcohol and the amount of alkoxylation, a variety of functional and non-functional hydrocarbons of varying molecular weights may be dispersed in water-based systems. Thus, the molecular weight of the starting alcohol may be chosen to afford a starting material having a number average molecular weight of from about 350 to about 2,000.

The alcohol starting materials are commercially available under the trade name UNILIN® alcohols from Petrolite Corporation, Specialty Polymers Group.

Both functional and non-functional polymers having a molecular weight of up to about 50,000 may be dispersed in water-based systems by the dispersants of the present invention.

Functional polymers which may be dispersed in accordance with the present invention and using the dispersants described herein, include UNILIN alcohols, oxidized polyethylene, chlorinated polyethylene, maleic anhydride polymers, olefin/maleic anhydride adducts, natural waxes such as beeswax, carnauba and candelila waxes and derivatives of high molecular weight alcohols disclosed in U.S. patent application Serial No. 159,143, filed February 23, 1988 of common assignment.

Non-functional hydrocarbons which may be dispersed in water-based systems in accordance with the present invention, and using the dispersants described herein, include waxes, hydrocarbon polymers, microcrystalline waxes and the like.

The present invention relates to two types of water-based ink additives systems. The first type of system is termed an "unsupported" system and the second type is termed a "supported" system.

The unsupported system is composed of a aqueous dispersion of the dispersants described in the present invention. A stable, unsupported dispersion may be prepared by the following procedure:

1. Determine the final solids content of the dispersion which is desired. The maximum solids content attainable will vary with the molecular weight and the amount of alkoxylation of the described dispersants.
2. The amount of water needed is weighed into an agitated dispersion vessel and the amount of dispersant needed is added to a clean, dry container.
3. The dispersant is heated to 15-20°F. above its melting point and, at the same time, the water is heated to 190°F.
4 Once both components are at the appropriate temperature, the dispersant is slowly poured into the water.
5. When all of the dispersant has been added to the water, the heat source is removed and stirring is continued for 2 to 3 minutes.
6. The dispersion is slowly stirred, cooling at the rate of 2-4°F. per minute. When the temperature reaches 140°F., the cooling rate may be increased or held constant until the desired pour temperature is reached. A stable dispersion results.

It should be noted that the conventional method of generating dispersions by adding molten polymer to hot water and shock cooling will not in most instances produce stable dispersions of the dispersants of the present invention.

A supported system is a dispersion of a functional or non-functional polymer in water together with the dispersants of the present invention. The method of

making the supported dispersion depends upon the melt point of the polymer being dispersed. Polymers with melting points above the boiling point of water will require the use of pressure equipment to make the dispersion. Lower melting point polymers can be dispersed under atmospheric conditions. Supported systems in accordance with the present invention may be prepared in accordance with the following procedure:

1. Heat water in a dispersion vessel with mechanical means of stirring or mixing.
2. Heat the polymer and dispersant of the invention in a vessel that can be used to pour heated materials into heated water.
3. The materials heated in Step 2 will need to be heated to +20°F. above the highest melting point of the materials used.
4. Remove the heated mixture from Step 2 and slowly pour the mixture into the heated water with adequate stirring to thoroughly mix.
5. After the heated mixture has been added to the water, remove the heating source from the vessel and quickly cool the sample with stirring to achieve the smallest particle size dispersion. A stable, small particle size dispersion results.

Powdered polymers may be added to the described water-based additive system in order to obtain proper slip and rub resistance characteristics in the formulated ink. The polymers which may be used include the functional and non-functional polymers and mixtures thereof described above, having a small, preferably micronized, particle size. Thus, the polymer additive should have a particle size of from less than 2 microns to about 20 microns. Preferably, the additives have an average particle size diameter of from about 5 to about 12 microns.

The selection of the proper dispersant as described will depend upon the polymers and additives to be dispersed in the water-based system. It has been found that the dispersants described in the present invention show superior dispersant properties as compared with other commercially available, but lower molecular weight, alcohols and allow achievement of higher solids level in the dispersion, i.e., dispersions may be obtained containing up to about 70% solids. The amount of dispersant used may be from about 0.001% to about 50%, preferably from about 5% to about 35% based on the total weight of the dispersion.

The following examples illustrate specific embodiments of the invention, including the best means for practicing the invention, but it is understood that the examples are illustrations only and the invention is not to be limited thereby.

EXAMPLE I

Preparation of an Unsupported Ink Additive System

Using the dispersion procedure described above, a 36% solids dispersion was made of 350 gms UNITHOX® 450 dispersant (a linear, ethoxylated primary alcohol having a molecular weight of 850 prepared by 50% ethoxylation of starting alcohol having a molecular weight of 425) in 715 gms water. The dispersion remains stable at room temperature after one year.

If desired, additives may be added to the system by slowly sifting the powdered additive into the system with stirring.

EXAMPLE II

Preparation of a Supported Ink Additive System

Using the dispersion procedure described above, a 50% solids dispersion was made of 450 gms of an ethylene/propylene copolymer of 700 molecular weight in 500 grams water using 50 gms of UNITHOX 750 dispersant (a linear ethoxylated primary alcohol having a molecular weight of 1,400 prepared by 50% ethoxylation of starting

alcohol having a molecular weight of 700). The resulting dispersion is a thick, stable paste.

As in the unsupported system, polymer additives may be included in the system by slow sifting of the powdered polymer into the dispersion under agitation.

In accordance with the invention, dispersions of polymers in water having up to about 70% solids content may be prepared using the dispersants of the present invention.

While the illustrative embodiments of the invention have been described here and above with particularity, it will be understood that various other modifications will be apparent and can be readily made by those skilled in the art without departing from the spirit and scope of the invention.

CLAIMS

1. A stable dispersion comprising water and a linear, high molecular weight, alkoxylated primary alcohol.

2. Dispersion of claim 1 which further contains a powdered polymer additive.

3. Dispersion of claim 1 which further contains a functional polymer.

4. Dispersion of claim 3 which further contains a powdered polymer additive.

5. Dispersion of claim 1 which further contains a nonfunctional polymer.

6. Dispersion of claim 5 which further contains a powdered polymer additive.

7. Dispersion of claim 1 which further contains a mixture of functional and nonfunctional polymers.

8. Dispersion of claim 7 which further contains a powdered polymer additive.

9. A printing ink containing the dispersion of claim 1.

10. A printing ink containing the dispersion of claim 2.

11. A printing ink containing the dispersion of claim 3.

12. A printing ink containing the dispersion of claim 4.

13. A printing ink containing the dispersion of claim 5.

14. A printing ink containing the dispersion of claim 6.

15. A printing ink containing the dispersion of claim 7.

16. A printing ink containing the dispersion of claim 8.

17. A dispersion substantially as described herein in Example I or II.

Published 1990 at The Patent Office, State House, 66 71 High Holborn, London WC1R 4TP. Further copies may be obtained from The Patent Office. Sales Branch, St Mary Cray, Orpington, Kent BR5 3RD. Printed by Multiplex techniques ltd. St Mary Cray, Kent. Con 1/87